A structure marker study for Pd_2Si formation: Pd moves in epitaxial Pd_2Si

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A sample with the configuration Si (111)/single crystalline Pd_2Si/polycrystalline Pd_2Si/Pd is used to study the dominant moving species during subsequent Pd_2Si formation by annealing at 275 °C. The interface between monocrystalline and polycrystalline Pd_2Si is used as a marker to monitor the dominant moving species. The result shows that Pd is the dominant moving species in the monocrystal.

I. INTRODUCTION

The dominant moving species[1] in silicides during silicide formations have been studied extensively by inert marker[2] experiments.[3] In general, the results for dominant moving species during silicide formation are the same for different marker experiments even though the marker may not be inert.[4] However, the dominant moving species results for Pd_2Si formation are very diverse.[4] Pd[5] or Si[6–8], or both Pd and Si[9–11] have been reported as the dominant moving species during formation of Pd_2Si. This discrepancy could be due to a high sensitivity of the dominant moving species during Pd_2Si formation to the presence of impurities, or to the microstructures of the sample, or to the annealing temperature. If this is so, then the result obtained from the marker is doubtful, because the marker can change the dominant moving species by its very presence as an impurity, or by changing the microstructures of the silicide.

In this study, we use samples with the configuration Si (111)/single crystalline Pd_2Si (Pd_2Si^c)/polycrystalline Pd_2Si (Pd_2Si^p)/Pd to study the dominant moving species during subsequent Pd_2Si formation. The Pd_2Si^c/Pd_2Si^p interface is used as a marker (structure marker) in this case. If two Pd atoms move across the structure marker, then the Pd_2Si^c layer gains one molecule of Pd_2Si. On the other hand, if one Si atom moves through the structure marker, the Pd_2Si^p layer gains one molecule of Pd_2Si. This structure marker has the merits that (1) there is no intentionally introduced impurity in the sample; (2) when measuring the thickness of each Pd_2Si layer by backscattering spectrometry (BS), the method is twice more sensitive to the Si flux than to the Pd flux, while by measuring the shift of the Pd_2Si^c/Pd_2Si^p interface with respect to the Pd surface, the method is more sensitive to the Pd flux than the Si flux, just like an ordinary inert marker is. (The shift of an inert marker in energy space of BS is due to the energy loss of the material transported past the marker and Pd has a larger stopping cross-section factor than Si.) We point out also that we have assumed that new silicide forms only at the Si/Pd_2Si or the Pd_2Si/Pd interfaces. However, this assumption is always needed in the explanation for inert marker experiments.

II. EXPERIMENTAL PROCEDURE

Commercially prepared *n*-type Si (111) wafers of resistivity 1.5–2.5 Ω cm were cleaned ultrasonically with trichloroethylene, acetone, and methanol and then etched in a 20% HF solution. After a 5-min etch, the wafer was rinsed in deionized water, oxidized in RCA solution ($H_2O_2 : NH_4OH : H_2O = 1 : 1 : 5$) for 5 min, and then etched in a 6% HF solution for another 5 min.

Immediately after preparation, the wafers were loaded into an oil-free *e*-gun evaporator. A Pd film of about 280 Å thick was evaporated on top of the wafers. The samples were then annealed *in situ* at 400 °C for 90 min to form Pd_2Si^c (pressure $\approx 2\times10^{-8}$ Torr). After the sample had cooled down to room temperature, Si ($\approx$140 Å, named "thin samples", or $\approx$450 Å, named "thick samples") and Pd ($\approx$770 Å) were sequentially evaporated. The final configuration of the sample was Si (111)/Pd_2Si^c/Si/Pd. During all evaporations the pressure was below 4×10^{-7} Torr and the rate was about 10 Å/s. Samples were then annealed to form Pd_2Si in a vacuum furnace (pressure about 5×10^{-7} Torr) at 275 °C for different durations. The silicide formation and marker location were analyzed with 1-MeV $^4He^+$ BS.

III. RESULTS AND DISCUSSION

Figure 1 shows 1-MeV $^4He^+$ BS spectra of thin samples annealed at 275 °C for (a) 0, (b) 4, (c) 8, and (d) 12 min. The circles are the spectra taken with the incident $^4He^+$ beam aligned with the ⟨0001⟩ direction of the Pd_2Si^c, and the lines are the random spectra taken with the incident $^4He^+$ beam 7° away from the aligned direction and the sample rotating during the measurement of those samples. The spectra for random incidence show that the Pd_2Si is growing during annealing. The spectra for aligned incidence show that the thickness of the Pd_2Si^p is fairly constant, while the thickness of Pd_2Si^c increases during annealing. This result proves that most of the new Pd_2Si formed at the Si (111)/Pd_2Si^c interface during the Pd_2Si formation, if it is assumed that new silicide can only form at the boundaries of the silicide layer (i.e., the Si/silicide and the silicide/Pd interfaces) and that the Pd_2Si^c/Pd_2Si^p interface is immobile with respect to the silicide lattice during annealing. The first condition is always assumed in the explanation for inert marker experiments. The second assumption can be roughly checked by annealing the thick samples at the same temperature. Figure 2 shows the spectra of the thick samples annealed for (a) 8, and (b) 21 min at 275 °C. As in Fig. 1 we use lines and circles to represent spectra for random and aligned incidence, respec-

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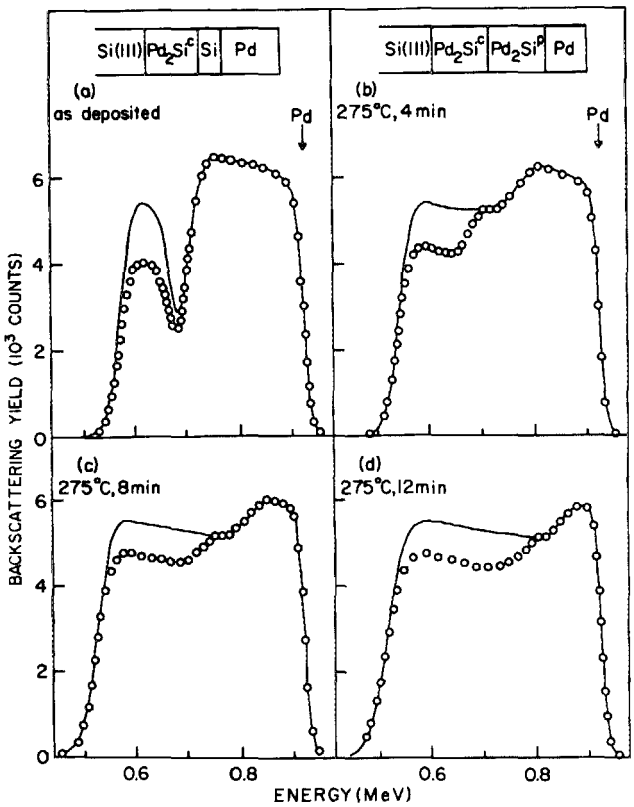

FIG. 1. Palladium signal of 1-MeV $^4He^+$ BS spectra of (a) an as-deposited thin sample [Si(111)/Pd_2Si^c/Si^c/Pd where the thickness of Si^c is about 140 Å] and those of similar samples annealed at 275 °C for (b) 4, (c) 8 and (d) 12 min. Circles represent spectra taken with the incident beam aligned along the ⟨0001⟩ direction of Pd_2Si^c, and solid lines represent spectra taken with the incident beam tilted 7° away from the aligned direction and the sample rotating during the measurement. For simplicity the Si signals are omitted. The detection angle is 170°.

tively. Figure 2 (a) shows that after 8-min annealing the Pd is fully reacted and that the sample configuration is Si/Pd_2Si^c/Pd_2Si^p. After 13 more minutes of annealing [see Fig. 2 (b)], the thickness of neither Pd_2Si layers has visibly changed.

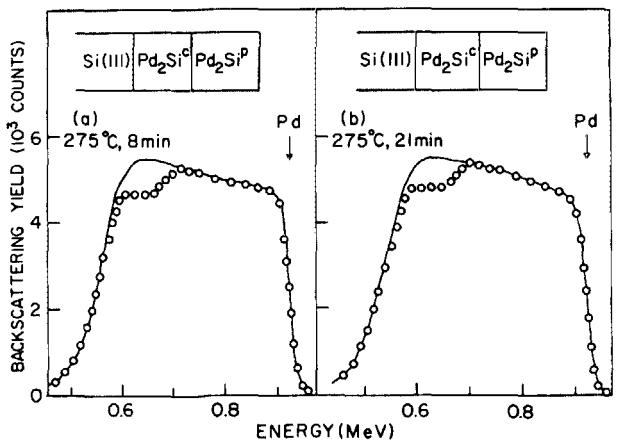

FIG. 2. Palladium signal of 1-MeV $^4He^+$ BS spectra of a thick sample [Si(111)/Pd_2Si^c/Si^c/Pd where the thickness of Si^c is about 450 Å] annealed at 275 °C for (a) 8, and (b) 21 min. Circles represent spectra taken with the incident beam aligned along ⟨0001⟩ direction of Pd_2Si^c, and solid lines represent spectra taken with the incident beam tilted 7° away from the aligned direction and the sample rotating during measurement. For simplicity the Si signals are omitted. The detection angle is 170°.

This suggest that the Pd_2Si^c/Pd_2Si^p interface is immobile during thin-sample annealing, i.e., the Pd_2Si^p does not recrystallize.

We thus conclude that the new silicide forms at the Si(111)/Pd_2Si interface which implies that Pd is the dominant moving species that diffuses through the Pd_2Si^c-Pd_2Si^p bilayer during the Pd_2Si formation. Since the Pd_2Si^c film is epitaxial, the motion of the moving Pd must be through the bulk of the Pd_2Si^c. We therefore suggest that in the sample with the configuration Si(111)/Pd_2Si^c/Pd, Pd is the dominant moving species. However, we need to admit the possibility that Si can move through the Pd_2Si when there are grain boundaries in the Pd_2Si. We thus cannot conclude that Pd is the dominant moving species in the sample with the configuration Si/Pd_2Si^p/Pd. In fact, it is shown that Si is the dominant moving species in the sample with the configuration Si/Pd_2Si^p/Pd.[7] We thus suggest that Pd_2Si^c acts as a barrier for Si flux and therefore Pd becomes the dominant moving species in our samples, i.e., samples with the configuration Si/Pd_2Si^c/Pd_2Si^p/Pd.

It should be noted that the interpretation of the experimental results reported here is based on some assumptions which we consider physically plausible. These are (1) no new silicide forms and no existing silicide dissociates during annealing at the Pd_2Si^c/Pd_2Si^p interface or within the bulk of these two silicide layers, and (2) the Pd_2Si^c/Pd_2Si^p interface is stationary with respect to the adjoining Pd_2Si lattices, i.e., the grains of the polycrystalline layer do not reregister onto the epitaxial layer during annealing. Without these assumptions, different interpretations of the experimental results are possible. However, similar uncertainties exist for other types of markers, too.

IV. CONCLUSION

We have demonstrated the possibility of using another type of marker (structure marker) to reveal the dominant moving species during a thin-film reaction. This marker has the advantage of not adding impurities in the investigated sample. The result shows that Pd is the dominant moving species through Pd_2Si^c during Pd_2Si formation. Additional experiments of this type measuring the dominant moving species for other epitaxial silicides would be desirable to further test the usefulness of the structure marker.

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[1]By "moving species" we mean the species that moves with respect to an inert marker (see Ref. 2).

[2]By "inert marker" we mean that a marker is fixed to the silicide lattice during the reaction and that does not interfere with the reaction processes.

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